COPPER CORROSION AND ITS CONTROL IN STARCH SYRUP MANUFACTURE[1]

BY K. A. CLENDENNING[2]

Abstract

Contamination of starch syrups with copper was kept to a minimum by mixing the acid catalyst with the starch slurry rather than with the priming water. Copper removal at the neutralization stage was promoted by protein impurities in the converted starch, high pH, and hot filtration. Decolorization with activated carbon removed less than 20% of residual copper, whereas acid-tempered bone char removed over 99%. The copper content of dilute syrups was determined without preparatory ashing by precipitation with salicylaldoxime.

Introduction

Little information has appeared in the literature concerning the corrosion of copper converters as a problem in starch syrup production. In view of the importance of the product as a foodstuff, consideration of the factors influencing both the introduction and removal of copper at successive stages of its manufacture appears desirable.

The present report deals with the protective action of starch hydrolysis products towards copper, the influence of protein content, level of pH adjustment, and filtration temperature on the removal of dissolved copper at the neutralization stage, and the relative effectiveness of bone char and activated carbon decolorization treatments in removing copper from the neutralized liquor. An adaptation of Riley's salicylaldoxime procedure for copper (15) was employed in this study, which permitted determination of the copper content of dilute syrups without preparatory ashing.

Copper and copper-containing alloys are quite resistant to dilute hydrochloric acid in the absence of oxygen and oxidizing constituents (9, p. 2; 17, p. 225). Oxygen is introduced with each batch of slurry, and it is known to stimulate copper corrosion by acid liquors (9, p. 2; 17, p. 225). The contents of the partially filled converter are highly acidic when the catalyst is mixed with the priming water, as recommended by many authors (1, pp. 181–187; 12, p. 215; 13; 18). A uniformly low acidity, on the other hand, is maintained during the filling operation by mixing the acid with the cold starch slurry before it enters the converter (4; 10, p. 284; 19).

Steam is blown into the converter contents throughout the filling operation, and, with thorough sparging, oxygen introduced with the priming water and slurry should be swept out before the pressure is raised. These considerations indicate that contamination of starch hydrolyzates with copper largely originates in the filling operation, and that it is promoted by introducing the acid with the priming water. Its dependence on the period of service of individual converters is also noteworthy; the experience of the industry has been that the copper content of successive hydrolyzates gradually diminishes, evidently through deposition of a protective coating of reversion products on the exposed metal surface.

Published information on the removal of dissolved copper from starch hydrolyzates is limited to that provided by McLachlan (11). According to this author, neutralization with sodium carbonate removes most of the dissolved copper, and copper precipitation from corn starch hydrolyzates is maximal at pH 5.1. He also reported less complete removal of copper by sodium carbonate precipitation from starch hydrolyzates than from solutions of copper in distilled water. The method used in determining copper in this work was not disclosed, and determination of pH by titration is unsatisfactory by present standards. It appeared necessary, therefore, to repeat McLachlan's work, as well as to investigate other aspects suggested by his published findings.

Copper Determination

A method for the determination of copper in dilute starch syrup was sought that did not require preparatory ashing. Color development in the presence of excess ammonia, as well as precipitation as copper thiocyanate (5, p. 200) proved quite unsatisfactory at low copper concentrations even in the absence of organic matter. Reif's microgravimetric method (14), in which salicylaldoxime is employed as precipitant, could not be used without modification over the greater part of the concentration range for which it was stated to be applicable.

Addition of excess salicylaldoxime reagent, as directed by Riley (15), to solutions containing less than 40 mgm. copper per liter resulted in turbidity, the intensity of which varied with the copper content. Flocculation occurred on standing with occasional agitation, and after 24 hr. in flowing tap water the supernatant liquid was rendered perfectly clear by precipitation, even at copper contents of 2 mgm. per liter. With this extension of time between addition of the precipitant and filtration, Riley's procedure gave quantitative recoveries from solutions of copper in distilled water at much lower copper concentrations than those that have previously been reported (Table I). Quantitative recoveries of copper were similarly obtained from 16° Bé. starch hydrolyzates of low copper content.

Completeness of precipitation was checked in routine applications with additional salicylaldoxime. Adequacy of washing the copper salicylaldoxime precipitate was established by re-extraction, drying, and weighing. In the

present applications, inorganic constituents were limited to sodium chloride, cupric chloride, and trace contaminants introduced with the starch. Previous work has shown that interference from these sources may be safely neglected

TABLE I

RECOVERY OF COPPER FROM DISTILLED WATER AND FROM STARCH SYRUP BY THE RILEY PROCEDURE, AFTER A ONE-DAY INTERVAL BETWEEN ADDITION OF PRECIPITANT AND FILTRATION

(Mgm. per liter)

Copper present	Distilled water, copper found	16° Bé. syrup, copper found
100.0	100.8	99.6
80.0	80.0	80.1
60.0	59.4	58.0
40.0	39.0	40.0
20.0	20.2	20.0
16.0	—	16.3
12.0	—	13.0
10.0	10.4	—
8.0	—	8.6
4.0	—	4.2

(7, p. 114). It was concluded that interference from nitrogenous impurities in the acidified salicylaldoxime medium could also be neglected, since no precipitation occurred in blank determinations on neutralized and filtered 16° Bé. starch hydrolyzates to which copper had not been added. The chief limitation of the method apparently is the error in weighing the precipitates when the copper concentration is below 10 p.p.m.

Results

Inhibition of Copper Corrosion by Starch Syrup

Table II provides data on copper corrosion by aqueous solutions at pH 1.8 and higher levels in the presence and absence of 16° Bé. starch syrup. The dilute starch syrup had a protective action at all pH levels, its reducing action evidently counteracting the known stimulating effects of oxygen. These results indicate that the rate at which traces of copper are brought into solution diminishes with the progress of individual conversions.

Inhibition of Gelatinization by Dilute Acid

Corrosion of new copper converters during the filling operation may be greatly reduced by mixing the acid catalyst with the slurry rather than the priming water. The feasibility of this practice depends largely on the type of holding tanks that are employed—if these are metallic, contamination of the product may then result from slurry acidification. Assurance is also needed that acidification does not promote slurry gelatinization.

TABLE II

CORROSION OF COPPER BY 16 BÉ. STARCH SYRUP AND BY WATER ADJUSTED TO DIFFERENT pH
LEVELS WITH HYDROCHLORIC ACID

(After 16 hr. contact at 100° C.)

pH	Sample	Wt. loss of copper test plates, mgm. per sq. dm.	Appearance of test plates
1.8	Water	306.0	Badly pitted and blackened
	Syrup	13.2	Tarnished
4.8	Water	15.6	Tarnished
	Syrup	8.8	Slightly tarnished
7.0	Water	11.4	Tarnished
	Syrup	8.2	Slightly tarnished

The data of Table III were obtained by microscopic observation of 0.8% starch slurries at 1° C. temperature intervals. Hydrochloric acid even at one-tenth normality raised the temperature at which marked swelling occurred

TABLE III

INHIBITION OF STARCH GELATINIZATION (GRANULE SWELLING) BY DILUTE HYDROCHLORIC ACID

HCl normality	pH	Gelatinization temperature, °C.					
		Wheat starch		Corn starch		Potato starch	
		Incipient	All large granules swollen	Incipient	All large granules swollen	Incipient	All large granules swollen
0	6.5	55	59	61	70	55	63
0.005	2.35	55	59	62	70	55	63
0.02	1.80	55	62	63	71	55	65
0.10	1.12	56	64	64	72	56	65

in all three types of starch. These observations are in agreement with those of Samec (16, p. 177), who reported increases in the gelatinization point of starch in dilute sulphuric and hydrochloric acid solutions: it was only with concentrations above 5 N with sulphuric and 1 N with hydrochloric acid that the gelatinization point dropped below that shown in water; acetic acid, on the other hand, decreased the gelatinization point at the lowest concentrations tested. This effect of acid has received little attention; it is a matter of interest that the catalyst of starch hydrolysis should inhibit the first stage of granule disintegration.

Factors Influencing the Removal of Dispersed Copper at the Neutralization Stage

The data of Table IV were obtained by adjusting an aqueous cupric chloride solution containing 200 p.p.m. copper to a pH of 1.8 with hydrochloric acid.

TABLE IV

INFLUENCE OF pH ADJUSTMENT WITH SODIUM CARBONATE AND OF FILTRATION
TEMPERATURE ON THE PRECIPITATION OF COPPER CHLORIDE FROM AQUEOUS
SOLUTION

pH	Filtration temperature, °C.	Filtrate copper content, mgm. per liter	Precipitation of copper, %
1.8 – 5.4	80	200	Nil
	25	200	Nil
5.85	80	90.7	54.7
	25	111.9	44.1
6.25	80	10.8	94.6
	25	33.0	83.5
7.00	80	3.6	98.2
	25	9.1	95.0
8.00	80	6.0	97.0

Sodium carbonate was then added to provide successively higher pH levels with accompanying precipitation of copper. Following filtration through Whatman No. 42 at 80° and 25° C., the filtrates were analyzed.

No precipitate was formed until the pH was brought above 5.4. The bulk of the copper was precipitated between a pH of 5.85 and 7.0, but it was not removed completely even at pH 8.0. Copper removal was consistently higher with hot as opposed to room temperature filtration. Judging from the observations of Hopkins and Beebe (8), and of Cloutier, Pelletier, and Gagnon (3), the copper precipitate is a basic complex with considerable affinity for water. With rising temperature, this unstable complex is rendered less soluble.

The experiments reported in Table V differed from the foregoing in that distilled water was replaced with (*a*) finished potato syrup diluted back to 16° Bé. and acidified, (*b*) freshly prepared 16° Bé. potato, and (*c*) wheat starch hydrolyzates. These solutions, which were prepared in glass-lined equipment (2), permitted observations to be made on the precipitation of copper by neutralization of starch hydrolyzates containing 0.007, 0.03, and 0.1% nitrogen respectively, expressed as protein on a wet basis. Prior to neutralization and filtration, 200 mgm. copper per liter was provided by the addition of cupric chloride.

Consistently less copper was removed from the diluted starch syrup at and above a pH of 6.0 than from distilled water. Copper precipitation was shown at a pH of 5.0 from the diluted starch syrup—below the point at which preci-

pitation began from aqueous cupric chloride solution.   Copper removal was higher at all pH levels from freshly prepared potato starch hydrolyzate than from finished syrup diluted back to 16° Bé.   Copper removal from the wheat

TABLE V

INFLUENCE OF pH ADJUSTMENT AND PROTEIN CONTENT ON THE PRECIPITATION OF COPPER FROM 16° BÉ. STARCH HYDROLYZATES

(Initial copper content, 200 mg. per liter)

pH	Copper removal, %		
	Finished potato syrup diluted to 16° Bé.	Potato starch hydrolyzate	Wheat starch hydrolyzate
4.0	0	32.6	63.0
5.0	24.8	51.5	85.0
6.0	36.7	81.2	92.0
7.0	89.0	94.8	72.5
8.0	91.3	96.1	45.9

starch hydrolyzate differed from that from all other solutions tested in that a maximum was shown at intermediate pH levels, as was reported for corn starch hydrolyzates by McLachlan (11).   The protein impurities in wheat starch promoted copper removal with pH adjustments to 4.0–6.0, and hindered copper removal at and above neutrality.

The amounts of copper removed on adjusting to pH 5.0 are of greatest practical interest since this pH appears to be generally suitable as a neutralization point in starch syrup production.   The removal of dissolved copper that was observed with filtration at 80° C. for this pH level showed important changes with the nature of the medium: from water, 0%; diluted starch syrup, 25%; potato starch hydrolyzate, 51.5%; and wheat starch hydrolyzate, 85%. The different solutions appeared in the same order with respect to copper removal at pH 4.0 and 6.0.   At pH 7.0 and 8.0 less copper was precipitated from the wheat starch hydrolyzate than from any other solution tested.

To determine completeness of copper removal at a lower copper concentration, wheat starch hydrolyzate was adjusted to a copper content of 20 mgm. per liter.   After neutralization to pH 5.0, decolorization by contact for one hour with 1% activated carbon on the juice weight and filtration at 80° C., the filtrate copper content was 4 mgm. per liter, representing 80% removal.

Removal of Residual Copper with Bone Char vs. Activated Carbon

Hinze (6) objected to the substitution of activated carbon for bone char decolorization of starch syrup because of its lesser ability to remove undesirable metallic salts.   To test the efficiency of these decolorizing agents with respect to copper removal, cupric chloride was added to neutralized and filtered

16° Bé. wheat starch hydrolyzates (pH 5.0, D.E. 50) to provide a copper content of 200 p.p.m. Samples of the dilute syrup were then mixed with activated carbon and acid-tempered bone char in proportions approximating those employed for decolorization (1% and 50% of the syrup weight respectively). After one hour at 80° C. the syrups were filtered and analyzed. Copper removal exceeded 99% with bone char, and the filtrates were water white and free of metallic taste. Approximately 17% removal was shown with activated carbon, and the thin syrup was light green and unpalatable. Under conditions favoring a high content of residual copper, bone char is superior to activated carbon as a refining agent.

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PRODUCTION OF SYRUPS FROM WHEAT, POTATO, TAPIOCA, AND WAXY CEREAL STARCHES[1]

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Abstract

Syrups prepared in semipilot plant equipment from wheat, corn, waxy corn, tapioca, and potato starches of low protein content were almost identical in taste and appearance. Differences in nature and amount of non-carbohydrate constituents did not necessitate modifications of the process. Wheat, corn, and waxy corn slurries hydrolyzed at approximately the same rate with 0.2% hydrochloric acid whereas potato starch hydrolyzed less rapidly. Contamination with 1.6% protein did not depress the hydrolysis rate but promoted foaming, turbidity, and bitterness. Loss of insoluble solids on the filter press averaged 1.25% for cereal and 0.3% for potato starch hydrolyzates. Complete decolorization of 14° and 30° Bé. syrup was effected by 0.5% activated carbon, based on the juice weight at each stage. Tap water promoted color development in the evaporator and inhibited color removal by active carbon. Color and fluorescence development in stored syrups was promoted by protein impurities, light, and tap water, and was strongly inhibited by sodium bisulphite. Syrups that remained colorless almost indefinitely were prepared from prime quality starches by using distilled water in the process and either acid-extracted carbon or bone char as decolorizing agents.

Introduction

The recent shortage of sucrose opened an unusually large market for starch syrup as an alternative sweetening agent. Supplies of raw material and the capacities of existing plants did not permit a large increase in the domestic production of corn syrup. As a result, corn syrup was imported from the U.S.A., Mexico, and Argentina, and commercial production of syrup from wheat and potatoes was undertaken in Canada for the first time.

These circumstances gave considerable impetus to studies of wheat starch manufacture, and several processes have now been described that provide starch of low protein content in high yield on a pilot plant scale (7, 10, 13, 14). The quality of commercial wheat syrups of both Canadian and American origin, however, has remained inferior to that of corn and potato syrups (6). Most of the wheat syrups examined by the authors were dark and became increasingly turbid during storage. Chemical analysis of these products indicated that the starches employed were heavily contaminated with protein, and that excessive amounts of sodium chloride and other salts were introduced in their manufacture (6).

The purpose of the present investigation was the provision of detailed information on the production of syrups from different types of starch by the batch acid hydrolysis process. The starches of wheat and potatoes received particular attention because of recurring surpluses in these products and their

recent use in syrup production. Tapioca starch was included because it usually is the least expensive starch on the world market. A comparison of ordinary and waxy corn starches was also judged of interest, since it permitted demonstration of the behavior of the amylopectin or branched component in the conventional conversion process.

Materials and Methods

The starches employed in this study were chiefly those whose composition and source are shown in Table I. Wheat starch slurries prepared from patent flour by the screening process described by Shewfelt and Adams (13), and

TABLE I

SOURCE AND COMPOSITION OF STARCHES

Starch	Source	Moisture, %	Ash, % d.s.	Fat, % d.s.	Protein, % d.s.
Wheat	Stein Hall and Co., New York, N.Y.	11.09	0.26	0.63	0.38
Wheat	N.R.C. pilot plant	10.83	0.12	0.60	0.34
Corn	Canada Starch Co., Cardinal, Ont.	10.48	0.05	0.64	0.32
Waxy corn	American Maize Products, Roby, Ind.	10.24	0.05	0.20	0.26
Potato	F. W. Pirie Co. Ltd., Grand Falls, N.B.	13.05	0.32	0.12	0.11
Tapioca	Stein Hall and Co., New York, N.Y.	10.17	0.08	0.27	0.14

concentrated to 16° Bé. by overnight settling, were also employed without further purification. To test the effects of protein contamination directly, prime quality wheat starch was blended with 100 mesh 'vital gluten'* and with patent flour to provide protein contents of 0.4, 0.8, and 1.6%. No attempt was made to exclude mineral impurities by the use of 'acid' starches since laboratory tests indicated that most of the bound acid was liberated as the starch disintegrated. As the various starches differed in acid-binding power, preparatory treatment with acid could lead to differences in free acid as hydrolysis progressed.

The extremely high viscosity of 23° Bé. waxy corn starch slurries at room temperature made it impossible to feed suspensions of this density to the converter. Conversion experiments on this starch were accordingly limited to 19° Bé. and lighter densities. Microscopic examination of the waxy starch revealed no evidence of incipient gelatinization or of gelatinous impurities, and nitrogen and pentosan determinations showed close agreement between the ordinary and waxy corn starch samples. Dilatancy tests also failed to reveal any distinction. The stiffness of the 23° Bé. waxy starch slurries may have resulted from granule adherence, of which there was some evidence in micromanipulation tests.

* *Supplied by Wheat Industries Ltd., Enfield, N.S.W., Australia.*

Dextrose equivalents and dextrose contents of the starch hydrolyzates were determined by the Shaffer–Hartmann and Sichert–Bleyer methods respectively, as modified by Zerban and Sattler (16). Optical rotatory power was determined at 20° C. on 100 ml. solutions containing 26 gm. solids and was expressed as specific rotation on a total solids basis. Slurry and syrup density measurements were made at 25° and 60° C. respectively with streamlined C.I.R.F. hydrometers*. Color was determined by transmittance measurements with the Evelyn colorimeter (Wratten filter 420) using colorless syrup of corresponding dextrose equivalent and density in setting the galvanometer (6). Fluorescence was determined by the method outlined by Pearce and Thistle (12). Moisture was determined by drying *in vacuo* on Filter-cel as directed by Cleland and Fetzer (4). Further details concerning the analytical methods employed are presented elsewhere (6).

It was found necessary to extract fresh bone char exhaustively with dilute hydrochloric acid before use on starch hydrolyzates: decolorization otherwise was very slow, and the decolorized syrup became very dark during evaporation. Three two-hour extractions with fresh lots of boiling 0.5 N hydrochloric acid followed by extraction with distilled water until the wash liquid remained neutral proved satisfactory and was adopted as a laboratory 'acid-tempering' treatment. This raised the carbon content from 8–9%, the usual level for sucrose refining, to 20–25%.

The processing equipment consisted of gravity filters, filter press, converter, slurry tank, and vacuum evaporator (Fig. 1). The bone char filters were constructed and operated in accordance with commercial practice. The glass-lined converter was equipped with steam jacket, steam sparger, and mechanical agitator. Ports were provided at the top for pressure gauges, thermometer well, sampling tube, air outlet, and slurry inlet, and a large gate-valve outlet at the bottom allowed rapid removal of the hydrolyzed liquid. A 5 gal. vessel equipped with an agitator was located above the converter, and the starch suspension was fed from it by gravity in filling the converter. Five-gallon earthenware crocks served as neutralizing vessels. The filter press was of standard 6 in. plate and frame construction. The evaporator consisted of a steam-jacketed copper kettle, of 5 gal. capacity, condenser, receiver, and vacuum pump.

It has been found most economical in the syrup industry to employ starch slurries having a density only slightly below the limit imposed by dilatancy, i.e., 22° to 24° Bé. The tendency of such heavy suspensions to form massive lumps when heated and the high viscosity and poor heat transfer properties of the paste necessitate special precautions in filling the converter. Even with starch of the highest quality, improper technique at this stage leads to off-flavor and aftertaste. The method of adding the hydrochloric acid is also important (5); with the present glass-lined equipment it was most conveniently introduced with the priming water. A concentration of 0.2%

* Obtained from Wm. Hiergesell and Sons, 295 Pearl St., New York 7, N.Y.
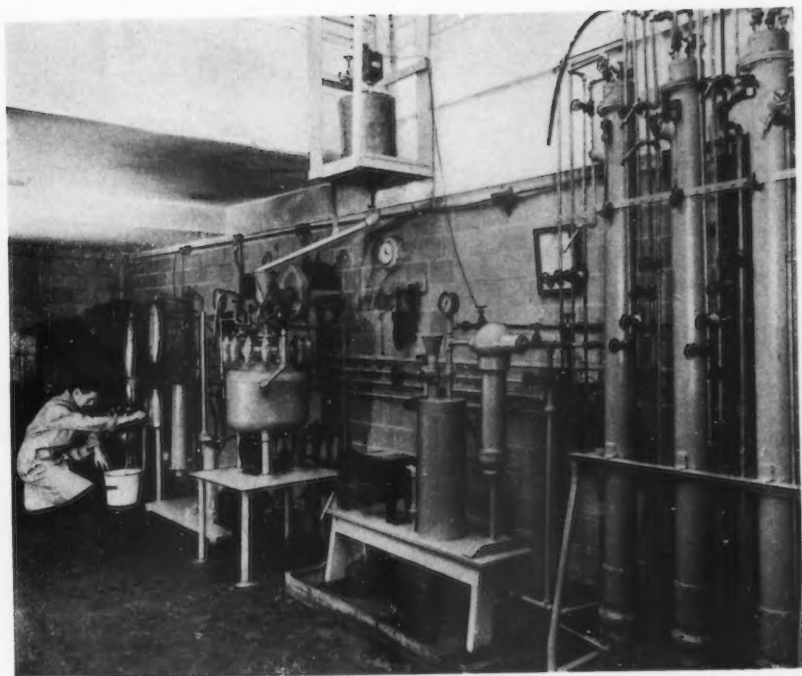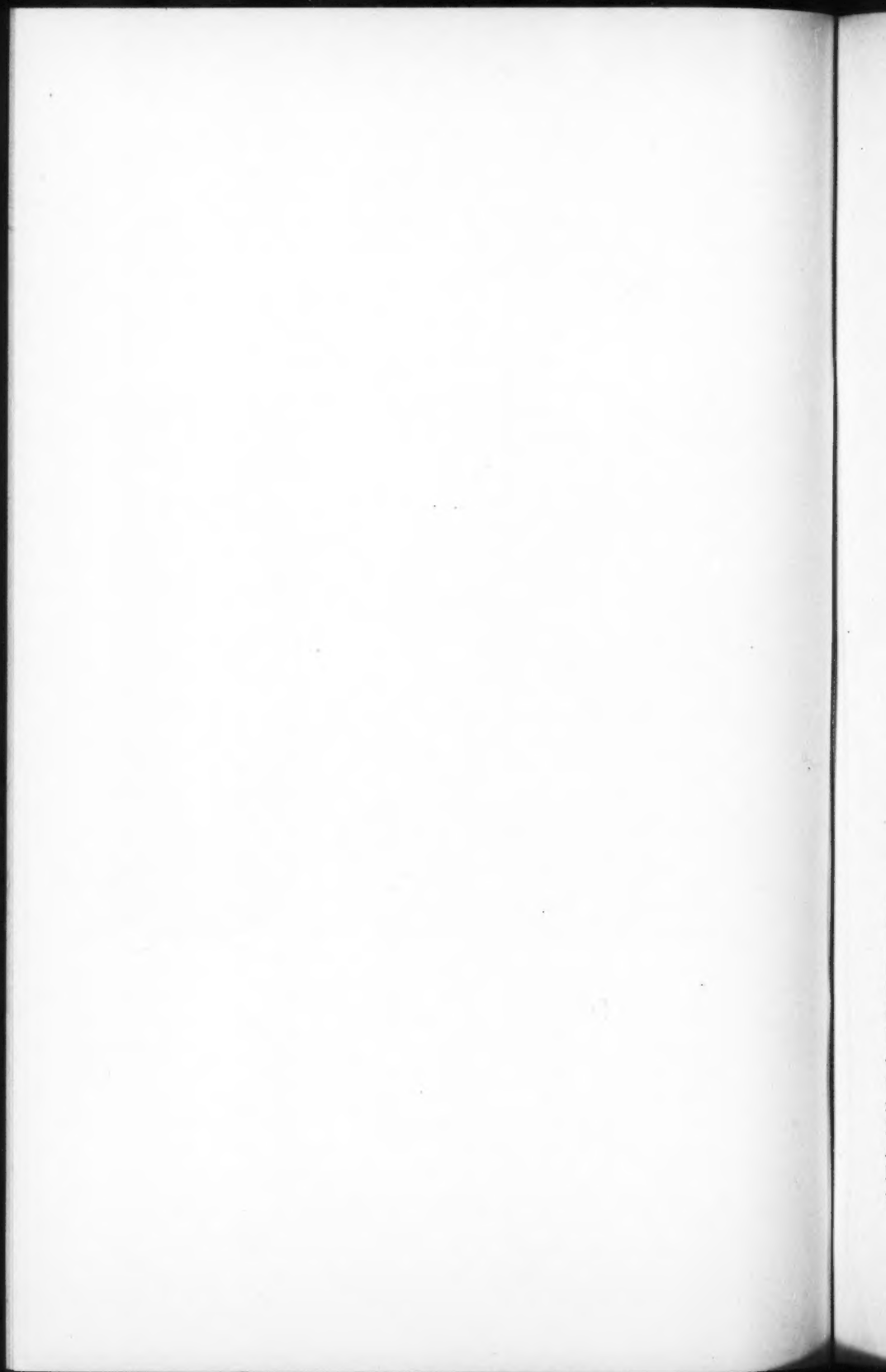
PLATE I

FIG. 1. *General view of the equipment.*

hydrochloric acid, based on the dry weight of starch, provides adequate acidification for 22° to 24° Bé. slurries, and this concentration was adopted as a standard condition. This method of expressing the acidity ensures uniformity in the sodium chloride content of the product when slurries of fluctuating starch content are employed.

At the outset of each conversion, sufficient 'priming' water is placed in the empty converter to cover the open-type steam coil: with converters of 2000 gal. capacity, approximately 100 gal. of water is required for this purpose. The water is brought to boiling by steam injection before addition of the 22° to 24° Bé. starch slurry is begun. During the filling operation, which must proceed continuously, slurry addition and steam injection are integrated so that boiling of the converter contents proceeds vigorously, with steam escaping freely from the air vent.

After the converter has been filled and swept out thoroughly with steam, the pressure is raised to approximately 35 p.s.i. The progress of each conversion must be followed by iodine tests because of the magnitude of interbatch differences in hydrolysis rate. Ten drops of iodine reagent (1 gm. iodine and 2 gm. potassium iodide in 250 cc. water) are added to a test tube containing 10 to 15 cc. of the cooled hydrolyzate. Shaking to distribute the iodine through the upper half of the sample provides maximum definition of color. It is particularly helpful to have reference samples on hand for the range 30 to 40 D.E. Iodine should be added periodically to fresh samples of the reference hydrolyzates for accurate comparisons. Hydrolyzates that were removed immediately after the disappearance of mauve coloration showed dextrose equivalent values of 38 to 42 D.E. with the present equipment, irrespective of starch type and purity. Two additional minutes at 35 p.s.i. provided hydrolyzates having D.E. values of 45 to 50. A D.E. value of 55 is regarded as the upper limit for the acid hydrolysis process because of the off-flavor and crystallization tendency of more completely hydrolyzed products.

The bulk of the sodium carbonate required for neutralization is added with continuous agitation as rapidly as the foaming tendency will permit. Gradual additions are then made, with periodic pH measurements, until a value of 5.0 to 5.1 is attained. In industrial practice, fatty impurities are removed in skimming tanks as described by Bartling (3). Hyflo Super Cel (0.1 to 0.2%, based on the liquid weight) is added to facilitate removal of flocculated proteins and other impurities on the filter press. Activated carbon (0.2 to 0.5%, based on the liquid weight) may be introduced with the filter aid either before or after neutralization, or may be added to the hydrolyzate after the bulk of the insoluble impurities have been removed by filtration. The carbon is removed on the filter press after approximately 20 min. contact at 80° C. Evaporation to 30° Bé. may be effected *in vacuo* or at atmospheric pressure. A further 20 min. treatment at 80° C. with 0.5% activated carbon and 0.1% Hyflo Super Cel on the 30° Bé. syrup weight removes the color developed during the first evaporation. The final filtration at this density must effect complete

removal of suspended impurities.   In evaporating the heavy syrup *in vacuo* to the final density of 42° to 43° Bé., control Beaumé measurements are most conveniently taken at the evaporation temperature of 140° F., a correction of 1.0° Bé. being added to obtain the conventional density value at 100° F. (9).

In decolorizing with bone char, the neutralized hydrolyzate is defatted and is freed of flocculated proteins by filtration with diatomaceous earth before being percolated through the gravity filters.   After evaporation to 30° Bé., the syrup is again decolorized with bone char, and filtered if necessary before its evaporation to final consistency.

Results and Discussion

Hydrolysis

Successive batches of 23° Bé. slurries converted at 35 p.s.i. with 0.2% hydrochloric acid showed large differences in hydrolysis rate (Table II).

TABLE II

EFFECT OF SLURRY DENSITY ON THE REPRODUCIBILITY OF WHEAT STARCH
HYDROLYSIS AT 35 P.S.I. WITH 0.2% HYDROCHLORIC ACID, D.S. BASIS

Conversion time, min.	Slurry density, °Bé.		
	23	18	12
	Mean dextrose equivalent of hydrolyzates, d. s. basis		
25	42.7	42.9	31.5
35	54.8	55.0	39.9
45	64.2	63.9	43.1
S.D.	3.8	3.8	1.3

With heating periods of 25 to 45 min., the standard error for 18 conversions was 3.76 dextrose equivalent units.   These differences were observed with wheat starch from a uniform lot after careful standardization of the filling operation, as well as of the conversion treatment at elevated pressure.   Batch differences of similar magnitude were also observed with other types of starch. Reproducibility and rate of hydrolysis were not affected significantly by mixing the hydrochloric acid with the starch slurry rather than the priming water.   Reproducibility was improved and the hydrolysis rate was diminished on reducing the slurry density to 12° Bé., the acid concentration being maintained at 0.2% of the solids content (Table II).   The heterogeneity and poor heat transfer properties of the reaction mixture evidently are responsible for the differences in hydrolysis rate observed between successive batches at high starch concentrations and for the existing lack of critical data on starch hydrolysis under these conditions.   These characteristics also are the principal obstacles that must be surmounted in the development of continuous conversion processes (11).

The crude wheat starch slurries obtained by the screening process (13) deposit solids slowly, and, as a result, the slurries that have been employed on an industrial scale have usually been of low and variable density. Table III

TABLE III

Effects of Starch and Acid Concentration on the Hydrolysis of Wheat Starch

Conversion time, min.	Acid conc'n.	Slurry density, °Bé.		
		23	18	12
		Dextrose equivalent values of hydrolyzates		
25	0.2%, d.s.	29.0	43.0	31.5
	0.015 *N*	29.0	46.1	71.7
35	0.2%, d.s.	43.7	55.0	39.2
	0.015 *N*	43.7	59.8	77.4
45	0.2%, d.s.	60.9	63.8	46.4
	0.015 *N*	60.9	72.2	79.2

demonstrates important effects of slurry density on the rate of hydrolysis. Rate of hydrolysis increases with decreasing slurry density when the amount of acid is maintained constant on a volumetric basis, and decreases when the acid is maintained at a constant percentage of the dry weight of starch. Use of dilute starch slurries necessitates hydrochloric acid concentrations in excess of 0.2% if the desired conversion is to be effected rapidly. The high sodium chloride content of many of the commercial wheat syrups examined by us (6) is attributed to this circumstance.

The lack of agreement between successive conversions on the same starch makes it impossible to provide satisfactory reference data for the hydrolysis of different starches under the usual conditions of syrup production. The data of Table IV indicate, however, that potato starch is more resistant to acid hydrolysis than tapioca or cereal starches. The tapioca syrups showed higher specific rotation values and lower dextrose contents than were observed with other starch hydrolyzates at similar dextrose equivalent levels.

With 23° Bé. slurries, the iodine end points were attained after 25 to 30 min. at 35 p.s.i. with the tapioca and non-waxy cereal starches, and after 35 to 40 min. with potato starch. The greater resistance to hydrolysis of potato starch was again apparent in experiments on 12° Bé. slurries (Fig. 2). Potato starch also shows greater acid-binding power, which Smirnov (15) has attributed to esterified phosphate in the amylopectin fraction. The concordance of the waxy and ordinary corn starch data indicates that absence of the amylose fraction has little effect either on the rate of reducing sugar formation, or on the composition of the product.

TABLE IV

ANALYTICAL DATA FOR HYDROLYZATES OF WHEAT, CORN, WAXY CORN, TAPIOCA, AND POTATO
STARCHES PREPARED WITH 0.015 N HYDROCHLORIC ACID AT 35 P.S.I.

		Conversion time, min.				
		20	25	30	35	40
Corn 23° Bé.	D.E. glucose $[\alpha]_D^{20}$	31.2 13.5 —	48.0 30.7 137.9	56.5 36.7 123.2	62.3 44.5 110.5	67.0 50.5 101.9
Corn 19° Bé.	D.E. glucose $[\alpha]_D^{20}$	36.3 21.4 —	44.2 28.3 144.2	50.6 33.4 134.8	56.3 37.2 124.4	61.1 42.9 117.7
Waxy corn 19° Bé.	D.E. glucose $[\alpha]_D^{20}$	26.7 14.3 —	36.8 21.0 157.5	44.1 28.0 138.4	50.9 31.5 136.6	56.1 38.0 125.5
Wheat 23° Bé.	D.E. glucose $[\alpha]_D^{20}$	29.0 13.5 —	38.7 20.2 147.7	43.7 23.0 137.8	48.3 29.1 127.7	55.8 37.0 117.3
Potato 23° Bé.	D.E. glucose $[\alpha]_D^{20}$	23.5 12.8 —	31.1 15.9 168.4	37.4 20.8 156.9	42.6 25.0 149.6	46.4 28.2 140.1
Tapioca 23° Bé.	D.E. glucose $[\alpha]_D^{20}$	37.1 13.7 179.6	40.0 16.6 174.8	47.1 22.0 167.2	52.8 25.5 158.2	58.0 32.6 150.0

Commercial wheat syrups of high protein content showed high sodium chloride contents (6), which might suggest that the protein impurities necessitated the use of additional hydrochloric acid. Table V shows that the hydrolysis rate under pressure was not reduced by the presence of 1.6% protein. The time required in reaching the iodine end point also was within the usual 25 to 30 min. range. It is therefore unnecessary to increase the acidity with this degree of protein contamination, which is far above the level at which syrup free of off-flavor can be obtained.

Syrups prepared from starches that were heavily contaminated with protein were consistently objectionable in taste and appearance. Bitterness and aftertaste were not removed by repeated passage through the bone char filters. Nitrogenous impurities cause troublesome frothing in the evaporator and affect the usefulness of the syrup in the confectionery and soft drink trades. Considerable haze also develops in finished syrups of high nitrogen content. When protein impurities are responsible, the latter fault can largely be corrected by diluting to 25–30° Bé., filtering off the flocculated impurities, and concentrating again to the usual consistency.

Purification of the starch before it enters the converter appears to be the only practical measure that can be taken to provide a syrup that is generally

satisfactory. Some improvement may be effected by the use of masking flavors, but the product is still inferior in taste and appearance to syrups prepared from 'hard' or 'prime quality' starch.
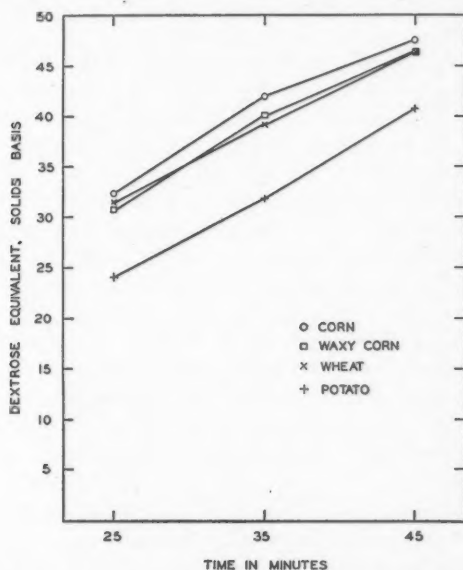

FIG. 2. *Hydrolysis of 12° Bé. starch slurries with 0.2% hydrochloric acid (d.s. basis) at 35 p.s.i.*

TABLE V

EFFECT OF PROTEIN CONTAMINATION ON THE HYDROLYSIS OF 23° BÉ. WHEAT STARCH SLURRIES WITH 0.2% HYDROCHLORIC ACID D.S. BASIS, AT 35 P.S.I.

The present data refer to wheat starch – 'vital' gluten mixtures

Conversion time, min.	Protein content of starch,%		
	0.4 (Control)	0.8	1.6
	Dextrose equivalent values of hydrolyzates		
25	44.5	41.6	45.1
35	57.3	59.5	56.8
45	64.8	71.6	61.4

Neutralization

In selecting a neutralization point for routine applications, a balance must be struck between filtration rate, filtrate clarity, and residual acidity. The adopted pH of 5.0 proved uniformly satisfactory on all starches; this indicates that the isoelectric point of the protein impurities is approximately at this acidity level. The filtration rate of wheat starch hydrolyzates drops off

sharply and the filtrates are turbid above a pH of 5.3. The filtrates are clear and filtration is rapid at pH values as low as 4.0. The protein dispersion that occurs on completely neutralizing cereal and potato starch hydrolyzates to pH 7.0 leads to serious frothing in the evaporator and also causes turbidity in the finished syrup.

Bartling (2) has prescribed the addition of 1½ gal. of 5% tannic acid solution to each 2000 gal. batch of corn starch hydrolyzate following neutralization and filtration. The effectiveness of this treatment in removing residual nitrogenous impurities was tested on crude hydrolyzates obtained from unrefined 16° Bé. wheat starch slurries. The above proportion of tannic acid solution was added to separate lots before and after the first filtration, with and without acetate buffering to pH 5.0. The nitrogen content of the finished syrup was not reduced by the addition of tannic acid to the unfiltered hydrolyzate, and was not affected by acetate buffering. Ten per cent reduction of the residual nitrogen content occurred with tannic acid additions following the first filtration. Higher tannic acid concentrations were not tested since the flavor of tannic acid was already evident in the product at the above level. Some improvement in taste quality may be obtained by the addition of tannic acid in the preparation of low quality syrups from impure starches, but this should be regarded as a direct result of its flavor rather than of its weak protein-precipitating action.

Protein and fatty impurities are the chief substances rendered insoluble by incomplete neutralization of cereal starch hydrolyzates, approximately 70% of the total nitrogenous impurities being removed at this stage. Potato starch contains less of these two classes of impurities, and losses of insoluble solids on the filter press are correspondingly smaller (Table VI). The data of

TABLE VI

LOSS OF INSOLUBLE SOLIDS ON FILTER PRESS (FROM 7 KGM. STARCH SOLIDS)

Source	Solids removed, gm.	% of total converted solids
Corn	86	1.23
Wheat	87	1.24
Potato	22.5	0.32

Table VI indicate that approximately 1% higher yield of syrup solids is obtained with root and tuber than with cereal starches. According to Bartling (2), the yield of corn syrup solids under industrial conditions varies from 101 to 104% of the dry starch weight.

Decolorization

The requisite amount of activated carbon can never be defined precisely because of the variations in requirements with differences in processing conditions and purity of raw materials. The amounts that have been prescribed

previously for complete decolorization range from 0.4% (8) to 4% or more (2) of the syrup solids.

The data of Fig. 3 illustrate the important differences in activated carbon (Darco S-51) requirements that were observed when tap water and distilled water were employed in the conversion. The hydrolyzates were prepared
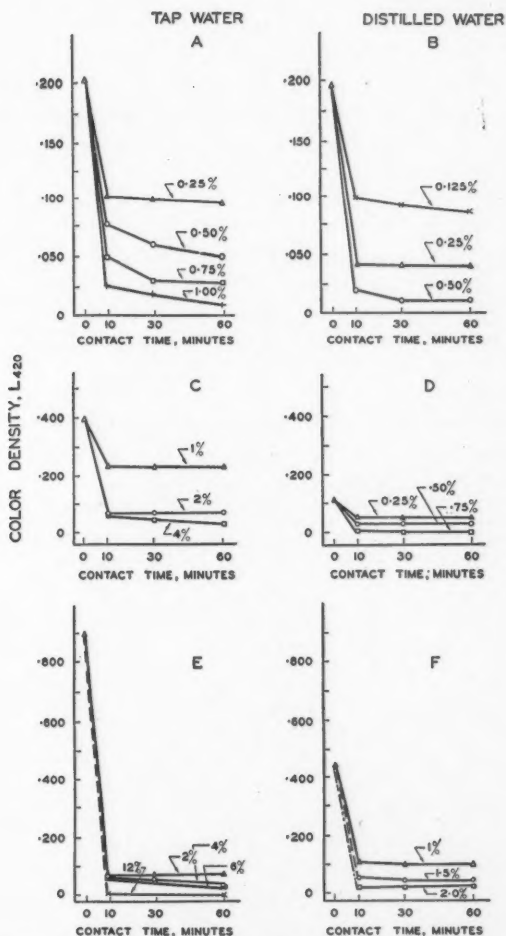

FIG. 3.   *Decolorization at 80° C. of wheat syrups prepared with distilled water and tap water.   Carbon treatments are expressed as percentages of the liquid weight.*

A and B, First decolorization at 14° Bé.
C and D, Second decolorization at 30° Bé.
E and F, Single decolorization at 30° Bé.

from wheat starch of high quality, which contained 0.35% protein. The amounts of carbon that were required in the first decolorization are shown in Fig. 3, A and B. Although the hydrolyzates were of similar color intensity, approximately twice as much carbon was required for equivalent decolorization at this stage in the presence of tap water. Considerably less color developed during evaporation to 30° Bé. when distilled water was used (Fig. 3, C, D). The quantity of carbon required at this stage (to 90% transmission at 4200) was reduced from 4% of the 30° Bé. syrup weight to 0.50% by the use of distilled water. Extending the contact time beyond 10 min. did not effect further color removal at this syrup density (Fig. 3, C, D). Four per cent and 1.5% carbon on the 30° Bé. syrup weight was required in the presence of tap water and distilled water, respectively, for equivalent decolorization by a single treatment at 30° Bé. (Fig. 3, E, F).

Employing distilled water, the over-all carbon requirements for colorless syrup production were 1.35% of the syrup solids with the conventional two-stage treatment, and 2.7% with a single decolorization at 30° Bé. The corresponding requirements in the presence of tap water were far greater (9.8 and 7.1%). The required quantity of activated carbon evidently is greatly increased by impurities introduced with the water used in slurry preparation. The importance of this effect cannot be adequately assessed from the present data, which are based entirely on local water. The results suggest, however, that a considerable reduction in the carbon requirement may be effected through the use of evaporator condensate or otherwise purified water.

The opinion expressed by Allen (1, p. 183) concerning the usefulness of bone char in starch syrup production is still widely held, i.e., "there has never been found a material that will exactly take the place of bone black in decolorizing and removing the bitterness from glucose (syrup) and corn sugar liquors".

In our experience, analytical data for syrups prepared with bone char and activated carbon have not indicated any marked superiority for the bone char syrups. No superiority was shown with respect to total ash (mainly sodium chloride), total nitrogen, or color development either on heating or during prolonged storage. Syrups possessing an off-flavor resulting from excessive protein contamination of the starch also were not noticeably improved by filtration over bone black. Bone char was found superior with respect to the adsorption of traces of dissolved copper and iron, as well as of the salts in industrial water that are responsible for storage haze in syrups prepared from starches of high quality. The very high efficiency of the revivification process largely accounts for the extensive use that continues to be made of bone char in starch syrup production. There may be other more elusive advantages gained through the use of char, but no clear-cut evidence of these was obtained in the present study.

Development of Color and Fluorescence in Stored Starch Syrups

A light amber color was developed during lengthy storage of syrups that were prepared from different types of starch and that had initially been decolorized with various brands of activated carbons or with bone char. Pronounced

storage color development was associated with a mild molasses-like flavor. Color formation could not be ascribed to a change in pH, and it was not influenced noticeably by the density or water content for the range 40° to 43° Bé., or by degree of conversion between 40 to 55 D.E. Color development also was not affected by extracting the hydrolyzate with ethyl ether; this indicates that the traces of hydroxy methyl furfural formed in the converter are of minor importance.

The syrups referred to in Table VII were prepared from tap water slurries of the commercial corn, wheat, and potato starches whose composition is shown in Table I, and of wheat starch to which gluten was added to provide

TABLE VII

EFFECT OF SULPHUR DIOXIDE ON COLOR DEVELOPMENT IN CORN, WHEAT, AND POTATO SYRUPS DURING TWO MONTHS' STORAGE AT ROOM TEMPERATURE

(All syrups initially colorless)

Source	Protein content, % d.s.	Color density, L420		
		SO_2 content, p.p.m.		
		0	200	400
Corn	0.11	0.097	0.039	0.034
Wheat	0.13	0.119	0.101	0.039
Wheat	0.48	0.297	0.264	0.135
Potato	0.04	0.056	0.021	0.013

1.6% protein. All syrups had dextrose equivalent values of 50 ± 2, were initially colorless, had a pH of 5, and a density of 42.0° Bé. at 100° F. Color development during two months' storage in diffuse light at room temperature was promoted by nitrogenous impurities and was inhibited by sulphur dioxide. Its stimulation by light is illustrated by Fig. 4. An increase in fluorescence
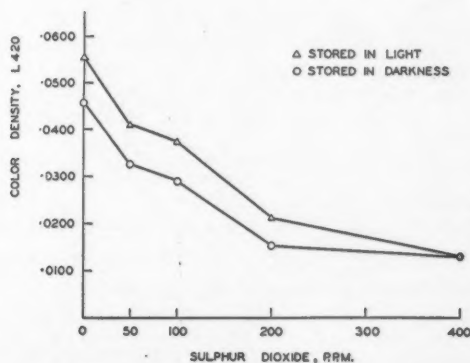

FIG. 4. *Effects of light and sulphur dioxide on color development in 42° Bé. potato syrup during two months' storage at room temperature.*

(Table VIII) was also observed during storage of wheat syrup, which showed general similarity to color development in that it was depressed by sulphur dioxide and was stimulated by a high content of nitrogenous impurities.

TABLE VIII

EFFECT OF NITROGENOUS IMPURITIES AND SULPHUR DIOXIDE ON THE DEVELOPMENT OF FLUORESCENCE IN WHEAT SYRUPS DURING TWO MONTHS' STORAGE

All measurements were taken on 20 gm. syrup diluted to 100 cc.

The fluorescence value for freshly prepared syrup was 8.0 units.

SO_2 , p.p.m.	Nitrogen content, as % protein	Fluorescence value
0	0.13	16.0
	0.48	28.4
200	0.13	15.2
	0.48	27.5
400	0.13	14.0
	0.48	22.2

The foregoing data indicate that storage color development is a result of Maillard reactions between reducing sugars and nitrogenous compounds. When acid-extracted carbon and distilled water were used in preparing syrups from the starches of Table I, the products remained free of color for six months and were only delicately tinted after one year's storage in diffuse light at room temperature.   Apart from the use of bisulphite and starch of low protein content, the most effective control measure apparently consists of excluding the catalytic impurities that can be introduced with the process water and carbon.

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SENSITIVITY OF CALCIUM SILICIDE SMOKE MIXTURES TO STATIC ELECTRICAL DISCHARGE[1]

By Archibald Gillies[2]

Abstract

Sensitivity to ignition of the three component system, calcium silicide, hexachloroethane, and zinc oxide, was studied. Apparatus is described and results plotted as isopotential lines on a trilinear chart. The investigation disclosed that mixtures of widely varying composition may be easily ignited and are therefore highly dangerous. Technological application of the deductions is discussed.

Introduction

During the recent war a number of fires accompanied by fatalities occurred in both Canadian and American plants preparing calcium silicide smoke mixtures. After one serious accident in Canada and another in the United States these mixtures were prepared in fireproof rooms, the machinery and handling devices being manipulated by remote control by workmen in adjoining rooms. This lessened the probability of fatalities, but did not reduce the loss of costly and non-replaceable equipment, the output of which was sorely needed by the armed forces. All possible precautions were taken to protect the lives of workmen in the plants while investigations were conducted to determine, if possible, the underlying cause of the fires. Sabotage was entirely ruled out and the cause, if not the actual means of initiation, sought within the three component system itself.

This paper describes the investigation of one aspect of the problem having a fundamental bearing on the fires. While no suggestions are offered regarding the initial means of ignition, it makes clear the underlying conditions that make initiation possible and propagation much more rapid than was expected with such mixtures.

Materials

The materials used in this work were taken from shipments received at the filling plants. The present study was made on what is officially known as Smoke Mixture 264A. This consists of:

Calcium silicide	10%
Hexachloroethane	45%
Zinc oxide	45%

When thoroughly blended this mixture burns relatively slowly. This behavior led to the misconception in smoke filling plants that the mixture was rather

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inert and quite safe to handle.   Such is true for the properly blended materials in the above mixture, but is not true for all possible combinations of the three components.

Methods of mixing used prior to this investigation had produced, during the process, compositions too close to the potentially dangerous ones, and the fires that took place are an indication that within the general mixture there were zones of highly sensitive composition.   This, no doubt, had occurred many times but only rarely were all conditions right for ignition of the batch. There is no reason to believe that subsequent methods of mixing eliminated all danger, but it is known that in Canada, following adoption of recommendations arising out of this investigation, no fires took place in mixers preparing Smoke Mixture 264A during the remaining years of the war.

Apparatus and Experimental

After some preliminary tests on a wide range of mixtures of the three components it became clear that there was a great difference in the ease with which some mixtures ignited and in the rate at which they burned.   Consequently, series of tests were made covering the range of mixtures that was of interest.

Use was made of a static electricity generator designed and constructed for the Explosives Laboratory by the Mechanical Engineering Division, N.R.C. (Fig. 1).
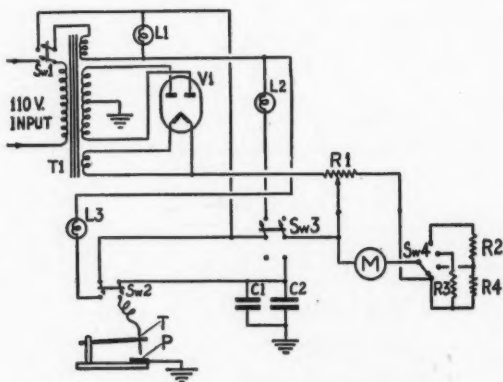

FIG. 1.   *Diagram of static electrical generator.*

$C1$ and $C2$ combined, constitute a 14 mf. condenser that can be charged to the limit of 400 v.   By proper manipulation of the resistances any desired voltage within the limits may be chosen.   By means of switch $Sw3$ the charged condenser is isolated from the power source, and is discharged through the sample on the grounded plate, P, when the pointer, T, is lowered into the sample.

The sample was prepared from calcium silicide ground as finely as possible in an iron mortar.   All three reactants were then ground together in an agate mortar.   As all components were of high quality they received no other pre-

PARTS FOR STATIC GENERATOR

Item	Description
$V1$	Tube—Type 80
$T1$	Transformer, Hammond No. 272
M	Voltmeter, 0–50 v.
$C1$	Condenser, 4 mf. 600 v. oil filled
$C2$	" 10 mf. " "
$R1$	Potentiometer 25K
$R2$	Resistor, 50K
$R3$	" 25K
$R4$	" $6250\,\Omega$
$Sw1$	Switch D.P.S.T.
$Sw2$	" D.P.S.T.
$Sw3$	" D.P.D.T.
$Sw4$	" 4 position selector
$L1$	Lamp, 6 v. (blue)
$L2$	" 6 v. (green)
$L3$	" 6 v. (red)
T	Pointer to discharge condenser
P	Grounded sample plate

paratory treatment.   Half-gram samples were placed upon the clean, grounded plate, P, and the condenser charged to a desirable potential.   A little experience made it possible to know approximately what voltage to try.   After the condenser was isolated from the power source the pointer, T, by means of its movable, insulating support, was lowered into the sample until it discharged.   If a sample ignited, a lower voltage was used and other samples from the same mixture tried until a voltage was reached at which the sample would not ignite.   Another sample was then examined usually at 5 v. above the previous potential.   If this ignited, the potential was lowered again by 5 v. and another sample tested.   If this failed to ignite, the previous voltage at which burning took place was taken as the minimum.   The percentage of calcium silicide was held constant while the other two components were varied and the minimum potential for ignition of each mixture determined.   From these data the minimum ignition potential of the most sensitive mixture for a fixed silicide content was chosen.   The data for 50% silicide content (Table I) will illustrate the method.

TABLE I

MINIMUM POTENTIALS REQUIRED FOR IGNITION OF MIXTURES CONTAINING
50% CALCIUM SILICIDE

Weight per cent			Minimum potential
CaSi$_2$	C$_2$Cl$_6$	ZnO	Volts
50	5	45	35
50	10	40	31
50	15	35	30
50	20	30	30
50	25	25	35
50	30	20	45

When plotted, these data give a minimum value of 28 v. This value was then plotted against 50% calcium silicide in Fig. 2 and the same procedure repeated for other silicide values. Plotting all the minimum values against silicide content gives the graph in Fig. 2.
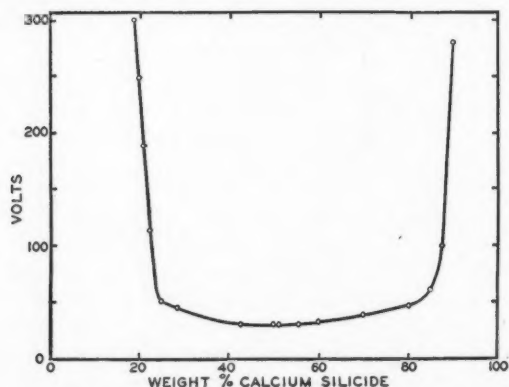
FIG. 2. *Minimum ignition potential versus calcium silicide content of the system hexa-chloroethane, zinc oxide, and calcium silicide.*

Results and Discussion

The information in Fig. 2 makes it quite clear that there is a wide range of mixtures with silicide content varying from about 20% to 90% that can be readily ignited. These mixtures are therefore highly dangerous if plant methods permit such compositions to occur in the process of mixing the six to seven hundred pound batches. All the information gathered from the aforementioned tests was used to plot isopotential lines on a trilinear chart (Fig. 3). An attempt was made to draw the curves in such a manner that they always represented the minimum potential required for ignition, i.e., the intervening areas may include some points having higher values but rarely any of a lower value. This gives at once a complete picture of the system so far as it was of

interest in the blending of smoke mixtures.   An area of high sensitivity lies around the region marked S.   By inspection of the isopotential lines this can be seen to be a wide region of varying compositions.   The boundaries of this area are quite sharp, the potentials rising quickly with but small change in the composition of the mixtures.   Thus, cross sections tend to resemble the curve shown in Fig. 2.

No values were determined for the area lying below the region marked S (Fig. 3).   This was not needed for technological application, but would have been desirable as a matter of interest.   However, the chart is very suggestive of the location of the uncompleted lines.
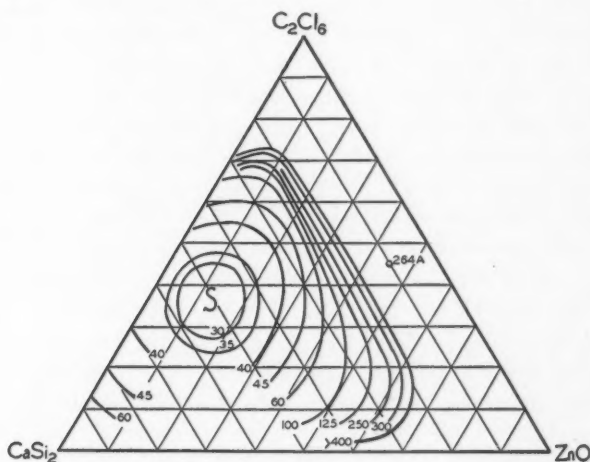
FIG. 3.   *Ignition potentials of the three component system hexachloroethane, zinc oxide and calcium silicide.*

If mixtures lying within the area of low ignition potentials could be avoided, the probability that fires would start would be greatly reduced.   This is possible by approaching the final composition (marked 264A on the chart) from the 50 : 50 zinc oxide – hexachloroethane mixture.   This 50 : 50 mixture was well blended, and with continued mixing the calcium silicide was slowly added.   This and slight modifications of this procedure were used to avoid, as much as possible, the highly dangerous compositions lying within the low potential area.   The lack of subsequent fires in 264A mixers would suggest that some benefit had been gained from the study of this system.

Acknowledgment

THE FP-54 AS A STABLE VOLTAGE AMPLIFIER[1]

By N. T. Seaton[2]

Abstract

A very simple method is given for operating the FP-54 Pliotron as a stabilized voltage amplifier with a grid current of less than 10^{-17} amp. The application of the method in the construction of a compact portable electrometer is discussed briefly.

General Discussion

The low grid-current characteristics of the FP-54 Pliotron make it an excellent electrometer tube. However, in most applications a difficulty is encountered in eliminating small voltage drifts in the associated circuit that result in instability. This difficulty is usually met by employing either heavy duty batteries and perhaps counter cells, or some form of bridge circuit. Considerable material has been written on the stabilization of the FP-54 as a current amplifier and a review of the various circuits employed has been given by Penick (5). Macdonald (3) has given an excellent discussion of d-c. amplifiers and the characteristics of the FP-54. Apparently little has been said however about the stabilization of this tube as a voltage amplifier, although it has been used as such by Müller and Shriver (4), Heidelberg and Rense (2), and others.

Inasmuch as the basic difficulty in stabilizing the FP-54 arises from the rapid change of space current with filament voltage, we will consider only stabilization against filament voltage variation. Stabilization against temperature variation in the other voltages can if necessary be obtained by the use of counter cells (7).

The basic circuit employed by the author is given in Fig. 1. For the plate voltage to be independent of the filament voltage we require $dE_p/dE_f = 0$ and thus that $dI_p/dE_f = 0$. Now consider operation at constant control-grid and plate voltage, then

$$\frac{dI_p}{dE_f} = \frac{\partial I_p}{\partial E_f} + \frac{\partial I_p}{\partial E_s} \cdot \frac{dE_s}{dE_f} , \tag{1}$$

and further

$$\frac{dE_s}{dE_f} = -R_l \cdot \frac{dI_s}{dE_f} = -R_l \cdot \left(\frac{\partial I_s}{\partial E_f} + \frac{\partial I_s}{\partial E_s} \cdot \frac{dE_s}{dE_f} \right) . \tag{2}$$

Solving Equation (2) for dE_s/dE_f, and defining $\partial I_s/\partial E_s = 1/R_s$, we obtain

$$\frac{dE_s}{dE_f} = \frac{-R_l}{1 + R_l/R_s} \cdot \frac{\partial I_s}{\partial E_f} . \tag{3}$$

Further defining $\partial I_p / \partial E_s = g_m$, and applying the condition $dI_p/dE_f = 0$, we obtain from Equations (1) and (3) the stabilization condition

$$\left(\frac{\partial I_s}{\partial E_f}\bigg/ \frac{\partial I_p}{\partial E_f}\right) \cdot \frac{g_m \cdot R_l}{1 + R_l/R_s} = 1. \tag{4}$$

The above condition, Equation (4), may be met for almost any values of filament and grid voltage; however, a filament voltage of about 1.2 v. would seem most desirable. The low emission of a microampere or so accompanying this filament voltage minimizes the grid current without reducing the plate current to too small a value. For most purposes all voltages can be obtained from ordinary radio dry cells.
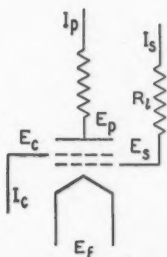
FIG. 1. *Basic circuit of the FP-54 voltage amplifier. For an appropriate choice of the operating conditions and of the space charge grid load resistor, R_l, the plate current becomes stabilized against filament voltage variation.*

Operation Conditions

The large variation in the characteristics of different FP-54's has been noted by various workers; Fig. 2 is an example of this from the present work. In some cases it has been possible to greatly simplify representation of the data (which can only be approximate in view of the above variation) by making certain assumptions.

It is evident[*] from the characteristics of Fig. 2 that the space current, I_{s_0}, is essentially saturated for $E_s > 2$ v.; although the issue is somewhat clouded in the case of Tube 2. Indeed, if we consider the distribution of voltage along the filament, we see that saturation begins to take place for an E_s of about 0.7 v. The first knee of the curves then corresponds to the 'end-effect' (due mainly to a temperature decrease) around the midpoint of the filament (inverted-V type), and should occur for an E_s of about $\frac{1}{2}(1.2$ v.$) + 0.7$ v. $= 1.3$ v., while the second knee corresponds to saturation being attained along the entire length of the filament and should therefore occur at 1.2 v. $+ 0.7$ v. $= 1.9$ v.

[*] *See, for instance, F. E. Terman, "Radio Engineering," 1937, Figs. 50a and 51.*

If we neglect the effect of small changes in E_f, per se, upon the distribution of I_{s_0} to the plate and space charge grid, and assume saturation, then it follows that we may replace $\dfrac{\partial I_s}{\partial E_f} \Big/ \dfrac{\partial I_p}{\partial E_f}$ by I_s/I_p and obtain as a useful approximation to Equation (4)

$$(I_s \cdot g_m/I_p) \cdot \frac{R_l}{1 + R_l/R_s} = 1. \tag{5}$$

An additional consequence of this assumption is that the space current, $I_s + I_p = I_{s_0}$, should be independent of the plate current, I_p, and consequently of the control-grid and plate voltages, E_c and E_p respectively. This approximation is valid over a very wide range of operating conditions.
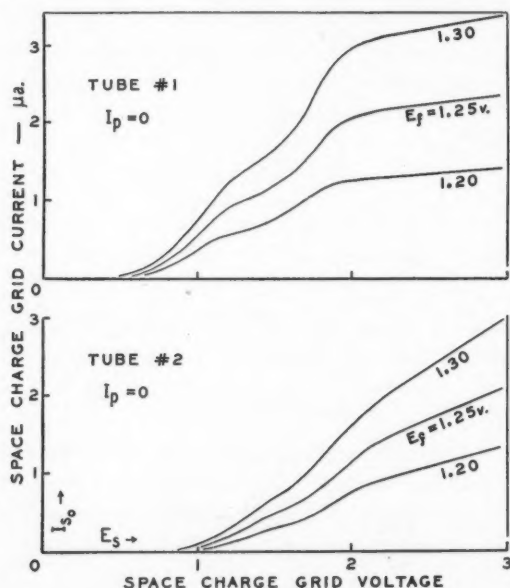

FIG. 2. *Space current characteristics of the FP-54, showing the variation that may exist between individual tubes. The space current, $I_s + I_p$, is essentially independent of I_p and hence can be represented by I_{s_0}.*

It is further of interest that the transconductance, g_m, may be regarded, first, as independent of the space charge grid voltage, E_s, for 1.6 v. $< E_s <$ 2.4 v., and second, as a function of I_p/I_s rather than of E_c and E_p.

In an actual circuit the presence of the space charge grid load resistor, R_l, effectively decreases the plate resistance, R_p, slightly for all I_s/I_p less than about 30, but leaves the amplification factor unchanged. These dynamic values are given in Table I. The effect may be shown mathematically if we take $(\partial I_{s_0}/\partial E_c)/I_{s_0} = (\partial I_{s_0}/\partial E_p)/I_{s_0} = 0.04$ μmho/μa. emission.

TABLE I

TYPICAL CONDITIONS FOR OPERATING THE FP-54 AS A STABLE VOLTAGE AMPLIFIER

(The E's are actual electrode voltages, not supply voltages.)

	Condition 1	Condition 2		Condition 1	Condition 2
E_f	1.2 v.	1.2 v.	I_p	0.1 μa.	0.1 μa.
I_f	65 ma.	65 ma.	R_l	1 meg.	1 meg.
E_s	2.0 v.	2.0 v.	R_p*	7 megs	10 megs
E_c	−1.5 v.	−4.5 v.	μ*	0.6	1
E_p	3.0 v.	5.5 v.	I_c	<5 × 10⁻¹⁷ amp.	<1 × 10⁻¹⁷ amp.
I_s	1.0 μa.	1.0 μa.			

* *Dynamic values.*

TABLE II

CONDITIONS AT A POINT OF FIRST ORDER STABILITY FOR WHICH THE SPACE CHARGE GRID VOLTAGE
IS BEYOND THE SECOND KNEE OF THE SPACE CURRENT CURVE (FIG. 2). AN INCREASE
OF FILAMENT AND PLATE CURRENT WILL LEAD TO A POINT OF SECOND ORDER
STABILITY. SEE ALSO FIG 5.

E_f	E_s	I_s	I_p	g_m	R_l	R_s
1.17 v.	2.2 v.	0.8 μa.	0.05 μa.	0.07 μmho	1 meg	6 megs

Satisfactory stabilization can be had for any reasonable grid bias, and representative conditions are given in Table I.   Control characteristics are given in Fig. 3.   The value of the grid current for condition 1 of Table I was
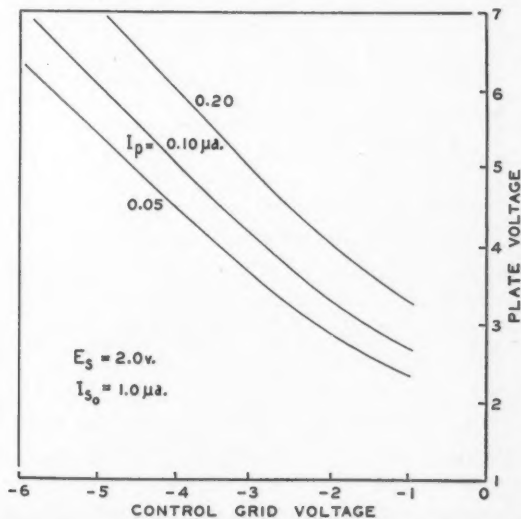

FIG. 3.   *Control characteristics of the FP-54.   These do not vary widely for different tubes.*

consistently obtained for both new tubes used by the author, and is considerably lower than expected on the basis of Macdonald's (3) results.

Stabilization

The most rapid method of obtaining stabilization is by experiment, and the following analysis should act as a guide. We consider the case where I_s/I_p is of the order 10. We may then regard R_s as independent of I_p (and hence E_p) and obtain it from Fig. 2. To attain the first order stabilization condition of Equation (5), it is best to choose first an approximately suitable value of R_l, and then to vary E_p, which controls only the first factor. The effect of E_p on the first factor of Equation (5) is shown in Fig. 4. The single control used to vary E_p, say a variable plate load resistor, further permits adjustment to a condition of second order stability.
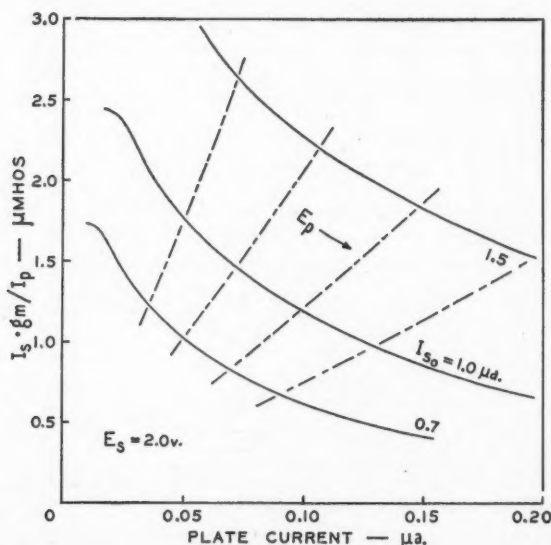

FIG. 4. *Plot of the first terms of the balance Equation (5). The dashed lines represent equal increments in E_p (or decrements in E_c) of about 0.3 v.; the actual value of E_p for a given I_p depends of course on E_c. (See Fig 3.) The different values of I_{s_0} are obtained by varying E_f. (See Fig. 2.) These characteristics vary considerably for different tubes.*

For second order equilibrium we require not only that Equation (4) be satisfied, but also that its derivative with respect to E_f be zero. For our considerations the latter condition may be put in the convenient form

$$\frac{\partial}{\partial I_{s_0}} (I_s \cdot g_m/I_p) = \frac{\partial}{\partial I_{s_0}} (1/R_s) + \frac{1}{2} (I_s \cdot g_m/I_p)^{-1} \frac{\partial}{\partial E_s} (-1/R_s). \quad (6)$$

The left side of Equation (6) can be obtained from Fig. 4 while both positive terms on the right can be obtained from Fig. 2. It is then seen that second order stability occurs for E_s in the region of the second 'knee' (Fig. 2), i.e., for $E_s \cong 2$ v.

Suppose for example we consider a specific tube, for which the stability curves of Fig. 5 apply. The conditions at the maximum of Curve A are given in Table II; these evidently satisfy Equation (5), the condition of first order
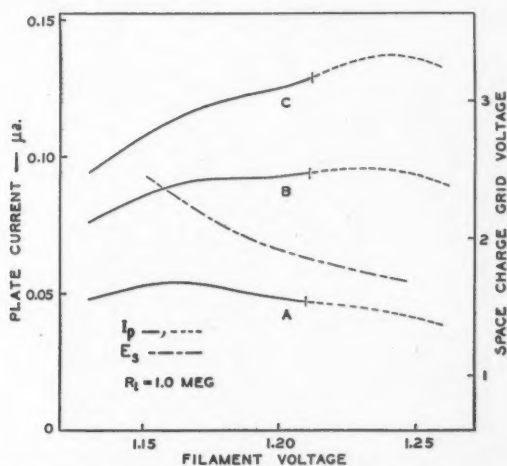

FIG. 5. *Typical stability curves showing that second order equilibrium is obtained by the appropriate adjustment of the plate current I_p. In general the sections (dotted above) corresponding to operation below the second knee of the I_s vs. E_s curves (Fig. 2) vary widely with different tubes, and although points of second order stability are often observed in this region, their determining factors would seem neither readily nor consistently found.*

stability. As I_p is increased, the maximum occurs at increased filament voltage, until finally the emission is such that $E_s \cong 2$ v. and the maximum becomes a point of inflexion, as in Curve B, giving second order equilibrium. Curve C shows the result of a still further increase in I_p. With second order stability it should be possible to vary E_f by 2% or so without changing I_p more than 0.1%. In an actual voltage amplifier circuit, the corresponding change in E_p is *limited* by the *plate* resistance, R_p, to about 1 mv. for the conditions of Table I.

The above discussion has been based on the use of E_p as a variable for obtaining stability. Although a variable R_l, with a *fixed E_p*, may be used to obtain first order stability, it cannot in general be used to obtain second order. However, if the tube is operated with essentially constant I_p (i.e., a large plate load resistor is used), a series of curves similar to those of Fig. 5 in the order A, B, C, can be obtained by increasing R_l (and decreasing E_f to keep E_s $\cong 2$ v.).

Application

As a stable voltage amplifier, the FP-54 is particularly suited for use as the input tube of negative feed-back amplifiers for the measurement of small currents.   Figs. 6 and 7 are the photograph and circuit diagram of an electro-
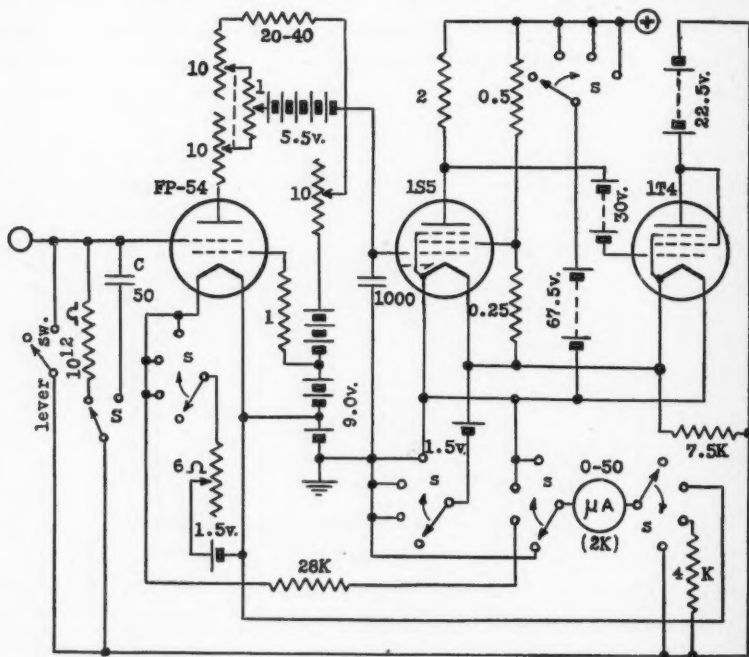

FIG. 7.   *Circuit diagram for the portable electrometer.   Resistances are given in megohms except as noted, capacities are in micromicrofarads.   Condenser C—vacuum mounted, guard ring.   Switch S—polished polystyrene stator.   Switch s—5 pole: off-on, fil. adj., range.*

meter employing it for this purpose.   As a direct-reading instrument, a full-scale reading at maximum sensitivity corresponds to 10^{-13} amp., while, as an integrating instrument, it corresponds to 5×10^{-12} coulombs.   Some special components required were the input lever switch, employing platinum contacts, and the switch S, which was constructed of standard wafer switch parts except for the polished polystyrene stator.   The condenser C was made from parts of a 50 $\mu\mu f$. Meissner 'Align-aire' condenser which were mounted in an evacuated Pyrex tube.   A grounded band of 'Aquadag' was applied to the outside of the latter to serve as a guard ring.

The use of negative feedback minimizes control-grid excursions, with the result that under actual operation, the conditions of stability are left undisturbed.   Further, although the effect of drift is not reduced by this procedure, the readings become essentially linear and independent of variations in tube
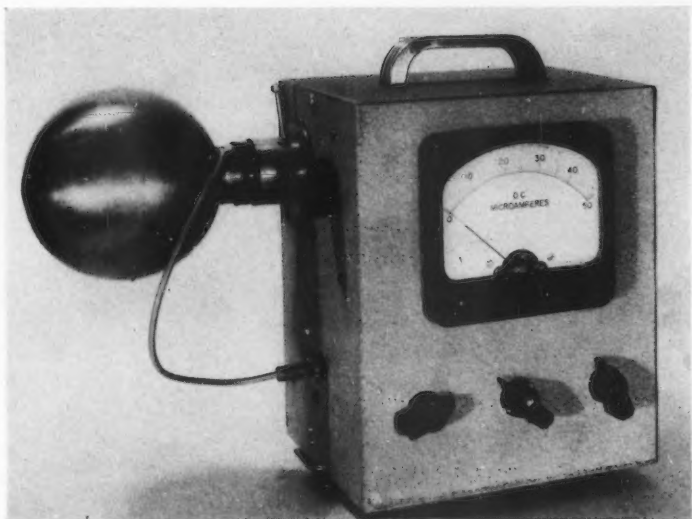
PLATE 1

FIG. 6. *A portable electrometer using the stabilized FP-54 circuit. A 10 cm. diameter spherical ionization chamber is attached to the input. At the upper left are the lever switch and the switch S of Fig. 7, while the controls below the meter are: the filament control, the range switch, and the fine zero-setting control. The coarse zero-setting control is adjustable from beneath the base.*

amplification.   The accompanying decrease in the resistive component of the input impedance greatly reduces the time constant of direct-reading instruments.   Further examples of negative feed-back amplifiers have been given by Vance (8), Roberts (6), Heidelberg and Rense (2) and Harnwell and Ridenour (1).

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